Deactivation of V$_2$O$_5$-WO$_3$-TiO$_2$ SCR catalyst at biomass fired power plants: Elucidation of mechanisms by lab- and pilot-scale experiments

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ABSTRACT

In this work, deactivation of a commercial type V$_2$O$_5$-WO$_3$-TiO$_2$ catalyst by aerosols of potassium compounds was investigated in two ways: (1) by exposing the catalyst in a lab-scale reactor to a layer of KCl particles or fly ash from biomass combustion; (2) by exposing full-length monolith catalysts to pure KCl or K$_2$SO$_4$ aerosols in a bench-scale reactor. Exposed samples were characterized by activity measurements, SEM-EDX, BET/Hg-porosimetry, and NH$_3$ chemisorption. The work was carried out to support the interpretation of observations of a previous study in which catalysts were exposed on a full-scale biomass fired power plant and to reveal the mechanisms of catalyst deactivation.

Slight deactivation (about 10%) was observed for catalyst plates exposed to a layer of KCl particles at 350 °C for 2397 h. No deactivation was found for catalyst plates exposed for 2970 h to fly ash (consisting mainly of KCl and K$_2$SO$_4$) collected from an SCR pilot plant installed on a straw-fired power plant. A fast deactivation was observed for catalysts exposed to pure KCl or K$_2$SO$_4$ aerosols at 350 °C in the bench-scale reactor. The deactivation rates for KCl aerosol and K$_2$SO$_4$ aerosol exposed catalysts were about 1% per day and 0.4% per day, respectively.

SEM analysis of potassium-containing aerosol exposed catalysts revealed that the potassium salt partly deposited on the catalyst outer wall which may decrease the diffusion rate of NO and NH$_3$ into the catalyst. However, potassium also penetrated into the catalyst wall and the average K/V ratios (0.5–0.75) in the catalyst structure are high enough to explain the level of deactivation observed. The catalyst capacity for NH$_3$ chemisorption decreased as a function of exposure time, which reveals that Brønsted acid sites had reacted with potassium compounds and thereby rendered inactive in the catalytic cycle. The conclusion is that chemical poisoning of active sites is the dominating deactivation mechanism, but physical blocking of the surface area may also contribute to the loss of activity in a practical application. The results support the observation and mechanisms of deactivation of SCR catalysts in biomass fired systems proposed in a previous study [Y. Zheng, A.D. Jensen, J.E. Johnsson, Appl. Catal. B 60 (2005) 253].

1. Introduction

Selective catalytic reduction (SCR) was developed for reducing NO$_x$ from stationary sources burning fossil fuels. However, the use of biomass for power generation has increased in recent years to reduce the net CO$_2$ emissions, and in some countries such as Sweden and Denmark, the SCR process is now being used on plants burning pure biomass or mixtures of biomass and others fuels such as coal, gas or oil. Unfortunately, it has been found that the SCR catalysts may deactivate much faster under biomass firing than when used on fossil fired systems [1–3]. The present authors investigated the operation of full-length monolith catalysts in a slipstream high-dust reactor installed at a straw-fired power plant [1]. A high deactivation rate of about 1% of the relative activity per day was observed when the power plant ran continuously.

Potassium, which is present in high levels in the fly ash of biomass fired systems, has been proposed as an important element for deactivation of SCR catalysts [1–3]. Although the potassium in full-scale systems is present as an aerosol of potassium chloride and sulphate, most previous investigations of SCR catalyst deactivation have been carried out in laboratory using wet impregnation with alkali oxides [4–7]. Our laboratory study using wet impregnation with potassium chloride and sulphate shows that also these compounds are strong poisons for the SCR catalyst [8].

Beside KCl and K$_2$SO$_4$ the aerosol in the flue gas from biomass fired power plants also contains minor amounts of sodium, phosphorous, and calcium, which are also known poisons to the SCR catalyst [4,7]. This makes it more difficult to interpret the

results of deactivation tests on full-scale plants, and so it is important to carry out more well-defined experiments where the catalysts are exposed to aerosols of single well-defined species. Only few such studies have been conducted in which catalyst powder or a small catalyst piece was exposed to aerosols of potassium compounds [9,10]. The exposure time in these experiments however, was only 30–100 h which is much too short to observe significant effects on the catalyst activity.

In this work, a layer of commercial KCl powder or ash collected from the SCR pilot reactor at the biomass fired Masnedø power plant [1] was loaded on one side of a series of catalyst plates placed in a lab-scale oven. The idea was to simulate the effect of the deposits observed previously in the pilot-scale tests [1]. Furthermore, full-length catalyst elements were exposed in a bench-scale reactor to aerosols of pure KCl or K_2SO_4 in long-term tests in order to investigate the relative contribution of these compounds to catalyst deactivation and compare the results with the observed deactivation in full-scale [1]. The results of these tests are reported and the deactivation mechanisms are discussed.

2. Experimental

2.1. Catalysts

Two types of V_2O_5-WO_3-TiO_2 catalysts obtained from Haldor Topsøe A/S were investigated, i.e., plates and full-length monoliths. The catalyst plates contained 1 wt.% V_2O_5 and about 7 wt.% WO_3 on a fiber reinforced titania (TiO_2) carrier. The active elements were uniformly distributed over the wall thickness. The plates had dimensions of 1.3 mm × 50 mm × 160 mm and were cut into 10 mm × 20 mm pieces for exposure and activity test. The corrugated-type monoliths were similar to the plates but had a V_2O_5-content of 3 wt.%. The dimensions of the monoliths were 75 mm × 75 mm × 500 mm and the hydraulic diameter of the channels was 6.44 mm. The total specific outer surface area of the monolith was 455 m^2/m^3 and the void factor of the monolith was 0.732. Table 1 shows that the BET surface area of the fresh monolith catalyst is about 59 m^2/g.

2.2. Exposure test for catalyst plates

Catalyst plates were exposed to a layer of commercial KCl particles (a mean diameter of about 360 μm, Merck, 104936) in a lab-scale quartz reactor. Fig. 1 shows the setup and the catalyst location. About 200 N ml/min compressed air passed through a water bath at room temperature to be saturated with $H_2O(g)$ (about 3 vol.%), and was then mixed with SO_2 to get a concentration of 1000 ppmv SO_2. Finally, the gas mixture passed through the reactor at 350 °C containing nine pieces of the catalyst plate. Only the three pieces in the middle were covered with a layer of KCl particles with a thickness of about 2 mm. The three plates in the upstream position were assumed to have no contact with the potassium salts or vapor and were used as baseline for comparison. The three plates in the middle were used to study the effect of the deposit layer on the catalyst surface. The last three plates in the
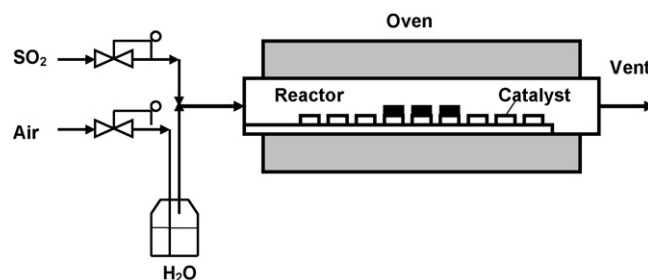
Table 1
BET surface area, BET and Hg-porosimetry pore volume and pore diameter of the fresh and the first KCl exposed samples

	Fresh	KCl aerosol exposed
Surface area (m^2/g)	59.43	55.13
Total pore volume (BET) (cm^3/g)	0.17	0.19
Total pore volume (Hg) (cm^3/g)	0.84	0.48
Average pore diameter (BET) (nm)	11.5	13.9
Average pore diameter (Hg) (nm)	97.6	81.7

Fig. 1. Schematic overview of the experimental setup for catalyst plate exposure test.

downstream position were used to investigate the effect of flue gas which had been exposed to potassium salts, i.e. the effect of potassium salt vapor.

In separate experiments catalyst plates were exposed to a 2-mm-thick layer of fly ash (contained about 55 wt.% KCl and 44 wt.% K_2SO_4) collected at the wall of the catalyst box just above the inlet of the catalyst mounted at the Masnedø SCR pilot plant [1]. In these tests no SO_2 was present in the gas in order not to promote further sulphation of the KCl in the ash.

After a certain time, the catalysts at the different positions were tested for activity in the fixed bed quartz reactor described elsewhere [8]. The gas for these activity tests contained 500 ppmv NO, 600 ppmv NH_3 vol.% O_2, and 5 vol.% H_2O in N_2 and the flow rate was about 1.2 N l/min. The activities of the catalysts were measured at 200 °C, 250 °C, 300 °C, 350 °C, and 400 °C, respectively. When NH_3 is in excess, as is the case in this work (NH_3/NO = 1.2), the reaction effectively reduces to first order with respect to NO and zero order with respect to ammonia [11–13]. The observed catalyst activity that includes the influence of external and internal mass transfer can then be calculated from [8]:

$$k = -\frac{F_{gas}}{m_{cat}}\ln(1 - X) \tag{1}$$

where F_{gas} is the gas flow rate (ml/s), m_{cat} is the weight of catalyst (g), and X is the fractional conversion of NO (%).

2.3. Exposure test for monolith catalyst

2.3.1. Bench-scale reactor

To expose the catalyst to poisons under more realistic conditions than in the laboratory experiments and study the effect of given compound, full-length monolith catalysts were placed in a bench-scale reactor shown in Fig. 2 and exposed to well-defined aerosols of KCl or K_2SO_4. Hot flue gas was produced by a natural gas burner and the NO level in the flue gas was adjusted by addition of NH_3 to the combustion air. A solution of the salt in distilled water (7.4 g/l KCl or K_2SO_4) was prepared and mixed several days before being added to the system. An aerosol of the salt was then generated by injecting the solution through a two-fluid nozzle into the flue gas close to the burner where the temperature was 1000–1150 °C. A bayonet heat exchanger was inserted into the main duct downstream the formation of the desired aerosol particles to cool down the flue gas before the un-lined steel tubes to avoid accelerated corrosion caused by the potassium compounds.

Upstream of the catalyst, NH_3 was added to react with the NO produced by NH_3 oxidation in the burner. The catalyst box was well insulated and heated by an electrical heating wire. The exposure temperature was kept at 350 °C and the temperature difference over the cross section of the catalyst box at the catalyst inlet was within 4 °C and the temperature difference between the catalyst inlet and outlet was kept less than 5 °C. A soot blower and a steel grid were installed 20 cm and 5 cm, respectively, above the
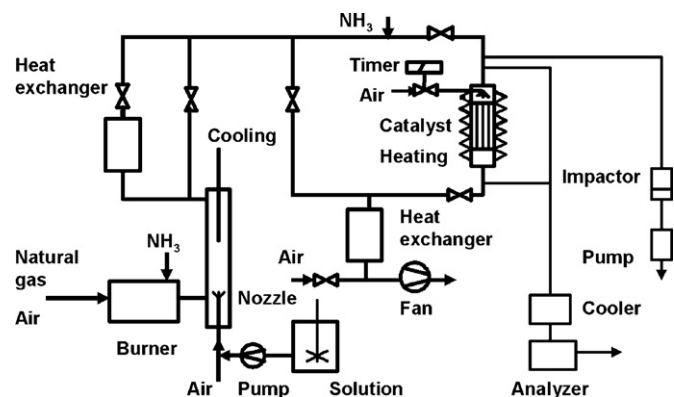
Fig. 2. Schematic drawing of the bench-scale reactor for catalyst monolith deactivation test.

catalyst to minimize plugging problems. The soot blower consists of a steel pipe with a diameter of 16 mm and a hole of 10 mm, a time controller and connects to compressed air at a pressure of 5 bar. Two additional soot blowers were placed just above the steel grid to blow away the particles deposited on the mesh. Soot blowing was carried out by 3–5 s of blowing with compressed air at an interval of 30 min. The total flow rate at the outlet of the burner was about 60 N m^3/h and the flow rate through the catalyst was kept at 40 N m^3/h by adjusting the bypass valve, which corresponds to a channel velocity of 6 m/s at 350 °C, similar to that of full-scale catalyst operation.

2.3.2. Activity measurement

Activities of the catalysts were measured in situ at 350 °C typically 2–3 times per day with a flue gas consisting of 500 ppmv NO, 600 ppmv NH_3, 6.5 vol.% O_2, 7 vol.% CO_2, and about 10–15 vol.% H_2O. As NH_3 is in excess, the observed catalyst activity can be approximated by an observed rate constant k' [8]:

$$k' = -\frac{SV}{A_p}\ln(1 - X) \tag{2}$$

where SV is the space velocity which represents the flow rate of the flue gas per unit volume of the catalyst element, A_p is the geometric surface area per unit volume (455 m^2/m^3), and X is the fractional NO conversion. To compare the deactivation rates of different catalysts, the relative activity was used, which was defined as:

$$\text{Relative activity} = \frac{k'}{k'_0} \tag{3}$$

where k' and k'_0 is the observed rate constant of the NO reduction reaction for the exposed and fresh catalyst, respectively.

2.3.3. Aerosol measurement

The aerosol particle concentration and size distribution were measured by a Berner-type low pressure impactor (Hauke model LPI 25/0.018/2). The impactor is a multistage device in which aerosol particles are separated into aerodynamic size classes with a range of 0.028–12.8 μm according to inertia characteristics. It consists of one pre-impactor stage for removal of large particles and 10 stages where particles are collected for subsequent gravimetric analysis. Aluminum foils greased with a thin layer of Apiezon H high-vacuum grease were used as collection substrate. The sampling flow rate was 23 N l/min and samples were taken from about 10 cm above the catalyst entrance through a straight cylindrical tube perpendicular to the flue gas duct (see Fig. 2). Prior to sampling, the gas bypassed the impactor for a period of time to approach steady-state conditions in the sampling line. Heating tape and mineral wool were wrapped around the

sampling tube and the impactor to keep a temperature of 120 °C in order to avoid condensation of water vapor.

2.3.4. Ammonia chemisorption

To investigate the mechanisms of deactivation, chemisorption studies similar to those conducted in our previous laboratory and pilot-scale studies [1,8], were made typically once per day. Flue gas produced without NH_3 addition to the burner and thus containing a low level of NO of about 25 ppm and with 600 ppm NH_3 added was first passed over the catalyst for a period of time to saturate the active sites. The effect of NH_3 saturation time was investigated and it was found that 30 min was sufficient to saturate the catalyst with NH_3 at the current conditions. After the saturation period, the NH_3 addition before the catalyst was shut off, and shortly after 500 ppmv NO was added to the flue gas through NH_3 combustion in the burner. Reaction between NO and chemisorbed NH_3 then took place and the amount of NH_3 on the catalyst was calculated from the amount of NO reduced.

2.4. Catalyst characterization

The distributions of potassium in the exposed catalysts were investigated at the Centre for Microstructure and Surface Analysis, Danish Technological Institute by SEM-EDX on a LEO 440 microscope. The samples were prepared by using an MT-990 rotary microtome. The samples were kept dry to prevent any dissolution, recrystallization, and removal of potassium compounds. Before analysis, the samples were covered with a very thin carbon film to become conductive. To compare the different spectra and samples, both carbon and oxygen are excluded from the analysis results and the amounts of other elements are recalculated on a carbon and oxygen free basis.

Surface areas by nitrogen adsorption at 77 K were measured on a Micromeritics ASAP 2000 automatic surface area and pore size distribution apparatus. About 0.4–0.6 g of sample was cut into 8 mm × 8 mm pieces and heated at 350 °C for 1 h before analysis. The total surface area was calculated by the BET method while the average pore diameter was calculated from the surface area and the BET pore volume. To determine the whole range of pore sizes, the pore diameter and distribution were also measured by Hg-porosimetry using a Micromeritics Autopore 9220.

3. Results

3.1. Deactivation of plate catalyst samples

Fig. 3 shows the activities of the catalyst plates at different positions after exposure of the catalysts in the middle position to (1) KCl particles at 350 °C for 2397 h including exposure to SO_2 in the period 0–670 h (lower figure), and (2) after exposure to ash from the Masnedø power plant for 2970 h (upper figure). For the catalyst plates exposed to KCl particles, the activities of the catalysts at the 'before' and 'after' positions were almost the same as the fresh sample indicating that no or little deactivation has taken place. The relative activities of the KCl exposed catalysts in the middle position were about 87% at 350 °C indicating that some deactivation has taken place. For catalyst plates exposed to Masnedø ash at 350 °C for 2970 h, no loss in activity was observed.

3.2. Characteristics of aerosol produced in the bench-scale reactor

To compare the aerosol concentration in the flue gas from the bench-scale reactor with that at the Masnedø power plant, the measured aerosol concentration was converted to a reference state of dry gas at 273.15 K, 101.3 kpa, and an O_2 concentration of 6 vol.%. Initially, it was planned to add at least half of the aerosol
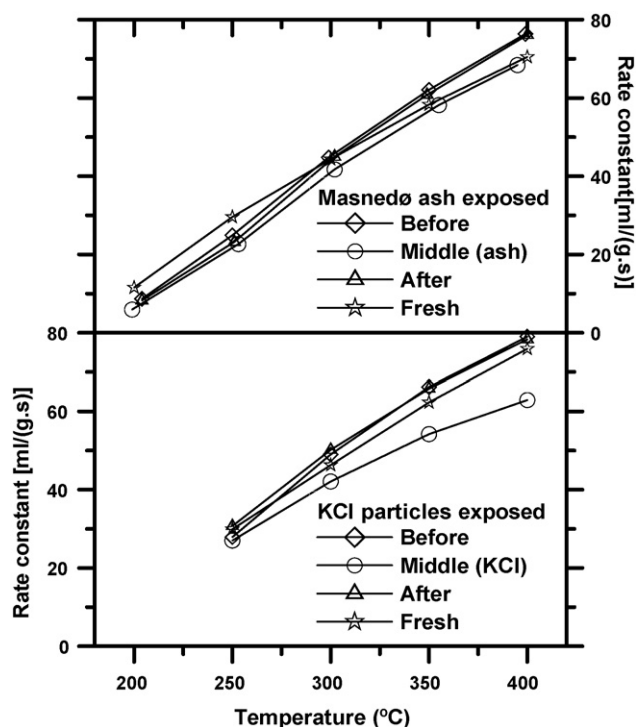
Fig. 3. Catalytic activities of the 1 wt.% V_2O_5-WO_3-TiO_2 catalyst plates as a function of temperature: (downside) catalyst plates exposed to the KCl particles for 2397 h including exposure to gaseous SO_2 for 670 h, (upside) catalyst plates exposed 2970 h to ash collected at the catalyst box just above the catalyst inlet at the SCR pilot plant installed at Masnedø straw-fired power plant.
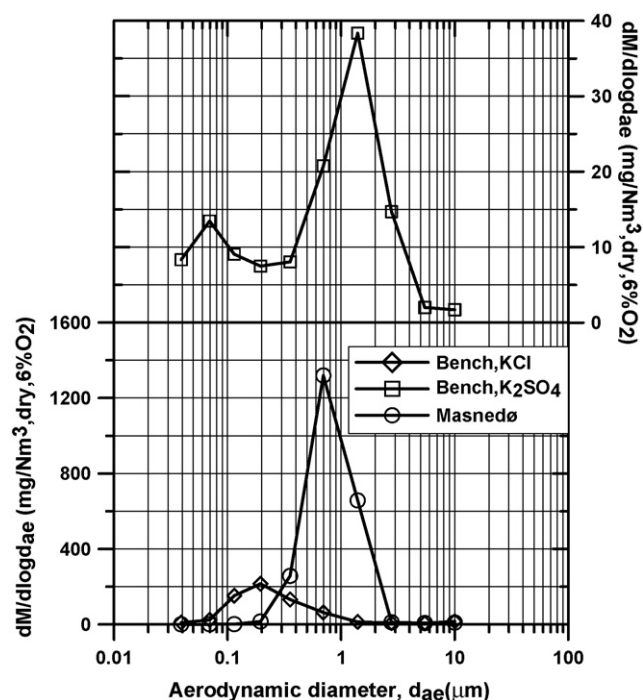

Fig. 4. Aerosol mass size distributions measured by the Berner-type multijet low pressure impactor at the entrance of the catalyst in the bench reactor, converted to the reference state, which is a dry gas at 273.15 K, 101.3 kPa, and an O_2 concentration of 6 vol.%. Upper figure: K_2SO_4 aerosol produced by adding 436 ml/h of 7.4 g/l K_2SO_4 solution 1120 °C. Lower figure: KCl aerosol produced by adding 420 ml/h of 37.3 g/l KCl solution at 1050 °C and aerosol measured at Masnedø SCR pilot plant.

load at the Masnedø SCR plant, which was about 580 mg/(N m³) [1]. When 835 ml/h of 37.3 g/l KCl solution was added to 60 N m³/h flue gas, corresponding to an aerosol load of 520 mg/(N m³), a concentration of 197 mg/(N m³) aerosol was measured at the inlet of the catalyst. Similarly 111 mg/(N m³) aerosol was measured at the catalyst inlet when nominally adding 260 mg/(N m³). In both cases only about 40% of the KCl particles reached the catalyst while the remaining were deposited in the reactor system before the catalyst.

When adding 835 ml/h of 37.3 g/l KCl the reactor could only run continuously for about 10 days. Then the heat exchangers became plugged and the pressure in the burner became too high and the burner automatically shut down for safety reasons. Therefore, the addition of KCl was decreased and only 436 ml/h of 7.4 g/l KCl solution corresponding to a calculated aerosol concentration of 53 mg/(N m³) was added. The gas temperature at the point of KCl solution injection was 1050 °C. This allowed continuous operation for about two months. The same loading was used for the addition of K_2SO_4, but the gas temperature was raised to 1120 °C to enhance vaporization.

To keep track of the aerosol concentration at the catalyst inlet, it was measured at a typical frequency of once per week by sampling 3.5 N l/min gas just above the catalyst inlet through a heated aerosol filter and weighing the mass change of the filter. The aerosol concentration increased over time from about 20 mg/(N m³) to 40 mg/(N m³) during the first exposure test of KCl aerosols. This was probably due to the accumulation of particles in the system that results in re-entrainment of the previously deposited KCl.

Fig. 4 shows the measured mass distributions of the aerodynamic diameters for KCl and K_2SO_4 aerosols in the bench-scale reactor and for the aerosol sampled at the Masnedø power plant. For the KCl and Masnedø power plant aerosols (lower figure), the

measured size distributions were unimodal. The geometric mean mass diameter was about 0.3 μm for KCl which is smaller than the 0.7 μm measured at the Masnedø SCR plant. However, similar mass mean diameter of 0.3–0.5 μm were obtained in other Danish straw-fired grate boiler [14].

The mass distribution of the K_2SO_4 aerosol is also shown in Fig. 4 (upper figure). In contrast to the KCl aerosol, there were two distinct peaks at 0.07 μm and 1.05 μm, respectively. The mass mean diameter was 0.55 μm. The different size distributions of KCl and K_2SO_4 aerosol could be due to the different aerosol dynamics of KCl and K_2SO_4. The concentration of the K_2SO_4 aerosol was almost constant at 20 mg/(N m³) for the first 2100 h, but then increased to 30 mg/(N m³) at the end of the test. Besides re-entrainment of previously deposited K_2SO_4 particles, another possible reason for the change in load could be the change of the nozzle. In the last exposure period, the nozzle was corroded and a new nozzle of the same type was inserted. The data in Fig. 4 were obtained using the first nozzle.

3.3. Deactivation of monolith catalyst by exposing to KCl aerosol

Two monolith catalysts were exposed to KCl aerosols at 350 °C and the catalyst activities as a function of exposure time to the flue gas are shown in Figs. 5 and 6. As shown in Fig. 5 the catalyst activity was constant during the first 340 h when no KCl was added. There was a decrease of the activity (9%) at 412 h which might be caused by the removal of the fresh catalyst from the reactor for about 130 h during maintenance of the burner. The catalyst was further removed for about 1300 h during a later maintenance of the reactor and aerosol measurement in the empty reactor. There was a sharp drop (12%) of the activity at an exposure time of 436 h when the catalyst was re-installed after KCl (load of 260–520 mg/(N m³)) had been added for 3 days to make the aerosol measurement. When KCl was added continuously at a level
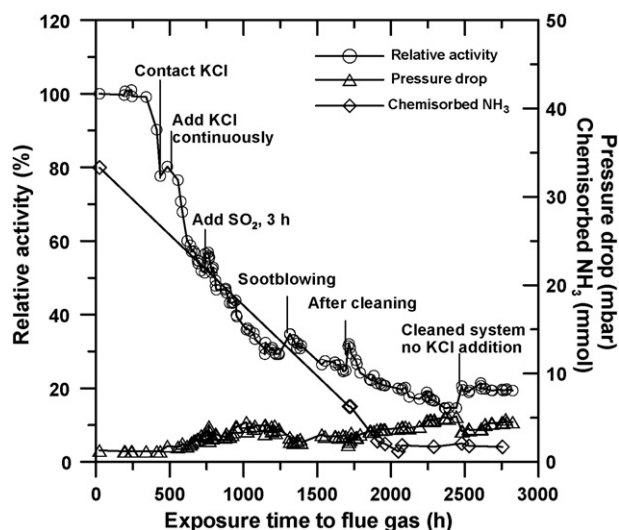
Fig. 5. Activities, chemisorbed NH$_3$, and pressure drop on the catalyst during the first KCl aerosols exposure test at 350 °C as a function of exposure time.
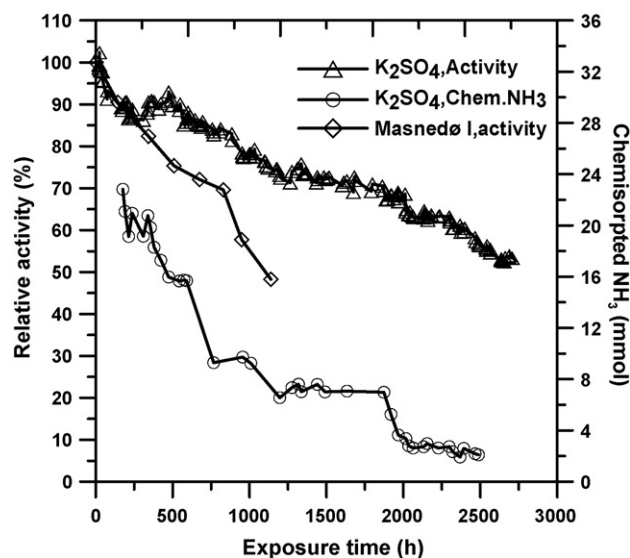

Fig. 7. Activities and chemisorbed NH$_3$ on the catalyst during the K$_2$SO$_4$ aerosols exposure test at 350 °C as a function of exposure time. Activities of catalyst exposed at Masnedø SCR plant for 1140 h at 350 °C are shown for comparison.

of 53 mg/(N m^3), the activity kept decreasing. At about 750 h, 1000 ppmv SO$_2$ was added for 3 h to check the system flow rate, and the relative activity increased from 51% to 56%. This is in good agreement with the Swedish study [15] where sulphation of the catalyst by SO$_2$ was conducted to regenerate the catalyst by increasing its acidity. The activity gain lasted for 3 days and then disappeared.

After about 1250 h, the pressure drop over the catalyst became high and automatic soot blowing every 30 min was initiated. The enhanced soot blowing also gave a rise of the activity of 5% probably due to cleaning of partly blocked channels. After exposure to the pure KCl aerosols for about 1830 h (total exposure time of 2440 h), the relative activity was only 18%. At the end of the test the reactor was opened and both the plugged channels of the catalyst and the reactor system were cleaned. The catalyst was tested for another 400 h without KCl addition and the relative activity leveled off at 20% as mentioned. The concentration of KCl aerosols in the bench-scale reactor was 10–20 times lower than in the SCR pilot plant at the

Masnedø straw-fired power plant. It is interesting to note that in spite of the much lower aerosol concentration in the bench-scale reactor during addition of pure KCl a deactivation rate similar to that at Masnedø of about 1% per day, was observed.

In the first test reported above, the final activity level was very low. A second test was carried out to investigate the repeatability of the experiment, and to confirm that catalyst deactivation stops when no further KCl is added, also when a significant part of the catalyst activity is still remaining. The soot blowing and the NH$_3$ chemisorption tests were carried out from the beginning of the second test. Fig. 6 shows that after exposing to KCl aerosols at 350 °C for 715 h the catalyst relative activity was about 69%, which corresponds to a deactivation of about 1.0% per day, in good agreement with the first test. There was also a fast decrease of the adsorption capacity for NH$_3$ on the catalyst as shown in Fig. 6. Then the system was cleaned and without addition of KCl the catalyst was tested for another 235 h. In this period the catalyst activity remained at about 69% and the amount of chemisorbed ammonia also leveled off.
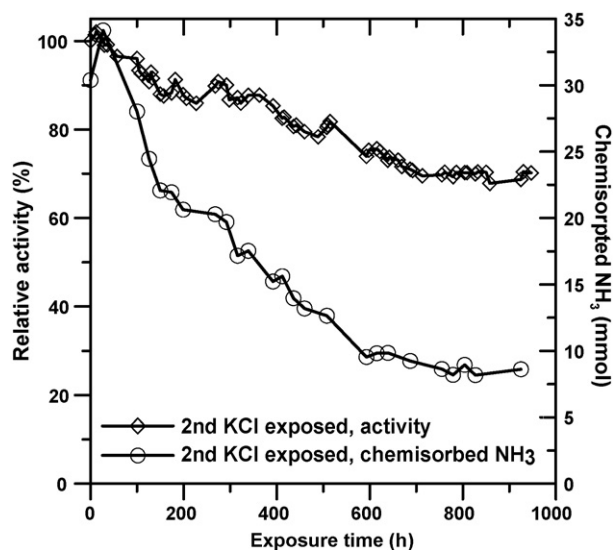
3.4. Deactivation of monolith catalyst by exposing to K$_2$SO$_4$ aerosol

The catalyst activity as a function of exposure time to K$_2$SO$_4$ is shown in Fig. 7. The relative activity decreased to 86% during the first 300 h, corresponding to a deactivation rate of 1.1% per day. As shown in a later section, this could be due to the deposited KCl in the system from previous test. Elemental analysis revealed that about 0.50 wt.% Cl was found in the catalyst structure. Apparently, the system has not been cleaned thoroughly enough between the tests. During the next 200 h, the relative activity fluctuated around 90%. Then the relative activity kept decreasing at a rate of about 0.4% per day; i.e. only 40% of the deactivation rate observed for catalysts exposed to KCl at a similar aerosol load and at Masnedø power plant. The pressure drop through the catalyst was almost constant at about 1.6 mbar except for a slight increase at the end.

Similar to the KCl aerosol exposure test, the catalyst capacity for NH$_3$ chemisorption decreased faster than the relative activity. Calculation of the effectiveness factor of the monolith shows that it is very low and the reaction takes place mainly close to the outer surface. Also, the fractional resistance to reaction by external mass transfer is around 70%. The active sites within the catalyst
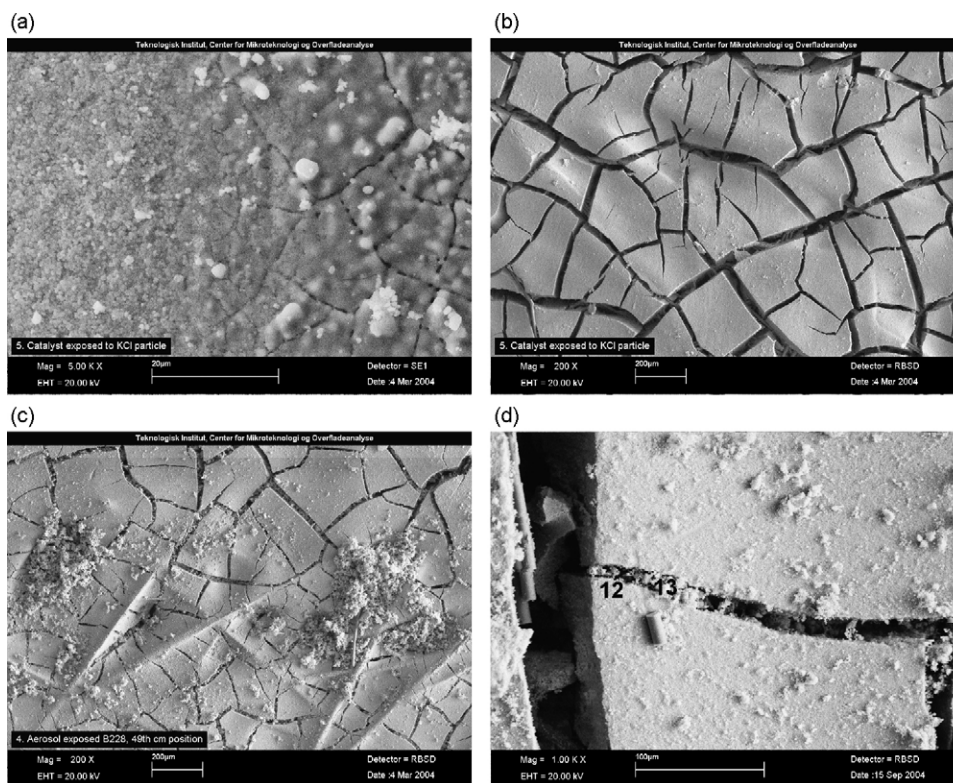

Fig. 6. Activities and chemisorbed NH$_3$ on the catalyst during the second KCl aerosols exposure test at 350 °C as a function of exposure time.

Fig. 8. SEM images of the exposed catalysts: (a) upper surface of the catalyst plate in the middle position exposed to a layer of KCl particles at 350 °C for 2397 h (with 1000 ppmv SO$_2$ for 670 h), (b) undersurface of the catalyst plate in the middle position exposed to a layer of KCl particles at 350 °C for 2397 h (with 1000 ppmv SO$_2$ for 670 h), (c) surface of monolith catalyst exposed to KCl aerosol in the bench-scale reactor for 1830 h (total exposure time of 2440 h) and (d) surface of monolith catalyst exposed to K$_2$SO$_4$ aerosol in the bench-scale reactor for 2707 h.

structure, although not participating in the SCR reaction, do react with potassium resulting in a faster decrease in the catalyst capacity for NH$_3$ chemisorption than the observed activity which is damped by the mass transfer resistances. Although there was a somewhat higher aerosol load in the last exposure period the deactivation rate did not increase.

3.5. BET and Hg-porosimetry measurement

As shown in Table 1 the BET surface area of the exposed catalysts was slightly smaller than those of the fresh samples. The Hg-porosimetry measurement shows that total pore volume and average pore diameter decreased after exposing to KCl aerosols, indicating that some macropores are plugged by KCl aerosols.

3.6. SEM-EDX analysis

Fig. 8a and b shows the SEM images of the upper and undersurface of the catalyst plate exposed to a layer of KCl particles at 350 °C for 2397 h (with 1000 ppmv SO$_2$ for 670 h), respectively. Few particles were found on the catalyst undersurface (Fig. 8b). These particles were probably from the catalyst material during the cutting of the sample before analysis. Elemental analysis showed that there was no potassium and chloride on the undersurface or in the dispersed particles, confirming that the few particles on the undersurface were from the catalyst matrix. It can be seen clearly from Fig. 8a that there were sintered KCl particles on the upper surface. There were several big particles with diameters of 2–4 μm and many small particles agglomerated on the surface. The average size of the commercial KCl particle was about 360 μm and the KCl layer was pressed onto the catalyst to avoid blowing it away by the air stream

in the reactor. There was almost no chloride in the catalyst structure, and potassium chloride was sulphated to potassium sulphate on the catalyst. Fig. 9 shows the potassium distribution along the catalyst thickness and it can be seen that potassium penetrated into about 10% of the wall thickness. However, for the catalyst exposed to ash collected at Masnedø, no potassium was found on either upper or undersurfaces.

Fig. 8c presents the surface analysis of the catalyst exposed to pure KCl aerosols for 1830 h (total exposure time of 2440 h) in the bench-scale reactor. There were some loose particles deposited on the surface and large pores were partly filled. SEM analysis at high magnification (not shown here) showed that the size of the particles were quite homogeneous and in agreement with the measurement by the low pressure impactor.

Somewhat surprisingly, the elemental analysis by EDX showed that the aerosols deposited on the first KCl aerosol exposed catalyst were mainly in the form of potassium sulphate. The average sulphur content at the surface (analysis down to a depth of 73 μm) was 3.35 wt.% on carbon and oxygen free basis, while the average sulphur content through the thickness of the wall was about 0.9 wt.%. Compared to the sulphur content in the fresh catalyst (about 1 wt.%) [16–18], the addition of sulphur to the catalyst by exposing the catalyst to 1000 ppmv SO$_2$ for 3 h was negligible. However, the promoting effect of surface sulphates was significant. When 1000 ppmv SO$_2$ was added for 3 h to calibrate the system flow rate, the activity increased from 51% to 56%. This is probably because sulphate species on the catalyst support interact with adsorbed water to form Brønsted acid sites on the catalyst surface under SCR conditions, promoting the adsorption of ammonia [19–21]. Studied by in situ Raman spectroscopy suggests that the SO$_2$ presence affects the molecular structure of catalysts with low vanadia coverage through driving
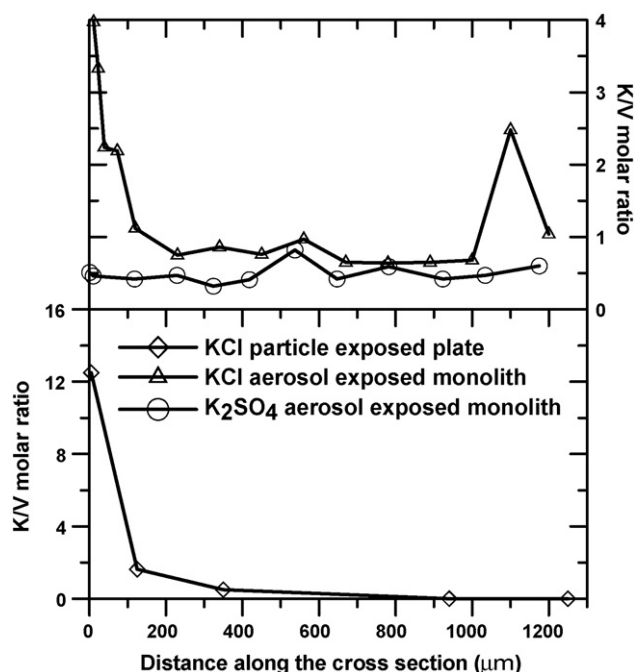
Fig. 9. Potassium distribution along the thickness of the catalysts exposed at 350 °C to KCl aerosol for 1830 h, K₂SO₄ aerosol for 2707 h, and KCl particles for 2397 h.

the dispersed vanadia species in a state of 'virtually' high surface density by crowding them together, thereby providing more adjacent V sites for activation of NH₃ in SCR reaction conditions [22]. In contrast to the distribution of sulphur, the contents of chlorine at the surface and in the catalyst structure were similar with an average content of about 0.33 wt.%.

Fig. 9 shows the profile of K/V molar ratio along the wall thickness of the first KCl aerosol exposed catalyst. There was a fast decrease of the K/V ratio from the surface into the catalyst structure. At a depth of about 200 μm, there was an average K/V ratio of about 0.75 in the catalyst structure. Such a K/V ratio is high enough for a significant chemical deactivation. Our lab-scale investigation [8] showed that the remaining activity of a 3 wt.% V₂O₅ catalyst doped with a K/V of 0.8 was about 10%. As discussed earlier, the remaining activity after exposure to the pure KCl aerosols for about 1830 h was only 18%, in reasonable agreement with the lab-scale data [8].

SEM analysis of the surface of catalyst exposed to K₂SO₄ aerosols for 2707 h in the bench reactor also showed loose particles deposited on the surface as shown in Fig. 8d. Elemental analysis showed that the sulphur content on the catalyst surface and in the deposit was 0.94 wt.% and 3.16 wt.%, respectively, indicating that sulphur level within the catalyst did not increase due to exposure to K₂SO₄. The cross-sectional analysis showed that the average K/V molar ratio in the catalyst structure was about 0.49, which was lower than that in the catalyst exposed to KCl aerosols for 1830 h (as shown in Fig. 9). There was about 0.3–0.5 wt.% Cl in the catalyst structure. As mentioned earlier, this could be due to exposure to KCl even in the K₂SO₄ test because the reactor was difficult to clean completely after the addition of the KCl.

3.7. Catalyst deactivation mechanisms

The catalyst deactivation can be caused by several mechanisms, namely, a decrease of the number of active sites, a decrease of the turn over frequency of the active sites, and loss of accessibility of the pore space [23]. The possible influence of each of these mechanisms in the deactivation of SCR catalysts when exposed to a potassium-containing aerosol is discussed as following.

3.7.1. Deactivation by fouling and channel plugging

The experiments and the SEM analysis showed that the catalysts had a high risk of fouling and channel plugging, and powerful and frequent soot blowing was necessary to keep the catalyst clean. Thus, fouling appears to be a more severe problem than in pure coal-fired applications. This could be due to the fine KCl and K₂SO₄ aerosols produced in the bench-scale reactor, which causes more particles to deposit by Brownian and turbulent diffusion. Furthermore there are no big particles in the flue gas to sand blast the catalyst surface. It was observed that plugging of channels takes place mainly close to the inlet. This may be caused by impaction of particles against the edge of the channel, which then accelerates the building up of deposits [24]. Additionally, KCl and K₂SO₄ have a lower melting point than typical coal fly ash and this may enhance sticking of the particles to the catalyst surface. It is clear that if a channel becomes plugged it will not contribute much to the activity. This may be a severe deactivation mechanism in full-scale where soot blowing cannot be carried out as frequent as in the present experiment. In the present experiments, channel plugging did not contribute much to the observed loss of activity, but fouling may have contributed to an unknown, but rather small extent.

3.7.2. Deactivation by poisoning and mechanisms of potassium penetration and accumulation

The SEM-EDX analysis shows that potassium penetrated into the catalyst wall and the NH₃ chemisorption measurement revealed that the Brønsted acid sites had reacted with poison and rendered inactive for NH₃ adsorption and subsequent reaction with NO. This chemical poisoning has been proposed by our previous study using potassium doped catalyst [8]. This mechanism can be supported by investigation of the potassium doped catalysts at molecular level [25,26]. In situ Raman spectroscopy revealed that potassium alters the vanadium surface species in the SCR reaction, lengthening the V=O bond. However, the detailed mechanisms by which the potassium penetrates the catalyst to the active sites are unknown. Based on the investigation at the Masnedø SCR pilot plant, several possible mechanisms for potassium accumulation and penetration were proposed by the present authors [1] and will be discussed below in the light of the results of the present work.

Deactivation due to diffusion of potassium vapor into the catalyst was ruled out in [1] since the calculated vapor pressures of KCl and K₂SO₄ at 350 °C indicate that this mechanism is much too slow. This is supported by the observation in [1] and the present work that without aerosols in the flue gas deactivation of the monolith catalysts due to potassium salt fouling layers does not take place. The fact that no deactivation of the catalyst plates in the 'after' position during the lab-scale exposure test further excludes deactivation by potassium vapor at 350 °C.

In [1] we also discussed whether the deactivation could be due to formation of liquid potassium-vanadium-pyrosulphates. Such species are the active phase in SO₂ to SO₃ oxidation catalysts, and could in principle be formed in the present systems thereby destroying the active sites in the SCR reaction. In full-scale tests SO₂ will always be present, but with the bench-scale reactor of this study, experiments in complete absence of SO₂ are possible. The results in Fig. 5 shows that the catalyst activity does decrease by exposure to pure KCl aerosols in the absence of SO₂, i.e. under conditions when the pyrosulphate mechanism could not have been active. The rate of deactivation, about 1% per day, is similar in full-scale and in the present experiments indicating that the pyrosulphate mechanism did not play a role in the full-scale tests either.

The slight deactivation of catalyst plates by direct contact with pure KCl or ash collected at the Masnedø SCR pilot plant indicates
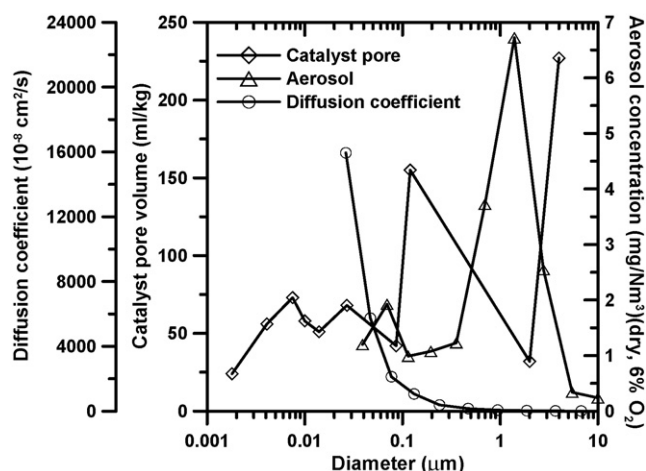
Fig. 10. Aerosol mass size distributions of K_2SO_4 aerosol at the catalyst inlet, pore size distribution of the 3 wt.% V_2O_5-WO_3-TiO_2 monolith catalyst, and the diffusion coefficient of the aerosols at 350 °C.

that the deactivation by deposits on the catalyst is a slow process. When KCl addition in the bench-scale reactor was disrupted, the catalyst relative activity and chemisorbed ammonia leveled off both at a low and high level of poisoning when the relative activities were 20% and 69%, respectively. This supports the findings of our previous work where it was observed that when the power plant ran few hours daily the catalyst activity leveled off [1]. If the pyrosulphates mechanism was active it would be expected that deposits on the catalyst surface would cause continuous deactivation. However, the results show that without an aerosol in the flue gas, no further deactivation takes place. This indicates that the potassium in the deposits on the catalyst wall is not capable of penetrating and deactivating the catalyst, or at least it is very slow.

As mentioned above a continuous flow of aerosol through the catalyst is required for deactivation, while the deposits of Merck KCl that contain rather large particles only cause slow deactivation (about an activity decrease of 0.1% per day with only one side contacting the deposit). This indicates that it is only the finest fraction of the aerosol that is involved in the deactivation. These particles are easily deposited due to their high diffusion coefficient, and the contact area with the wall, per mass of aerosol will be large. Fig. 10 shows the aerosol diffusion coefficient at 350 °C, the distribution of the catalyst pore size and the size distribution of K_2SO_4 aerosol produced at the bench reactor. The fine aerosol particles may directly diffuse into the catalyst structure since there is some overlap between the size distribution of the fine aerosols and pore sizes of the catalyst. This mechanism is further supported by a recent Swedish study [27]. They suggested that mainly alkali in ultra fine particles (<100 nm) in the flue gas caused the alkali accumulation on the catalyst samples exposed to the flue gas from biofuel and peat fired boilers. The catalysts investigated in our work use fiber reinforced TiO_2 as carrier and have larger pores compared to extruded or plate type catalysts. It is expected that fine particles diffuse into the large pores (>1 μm) of the catalyst used in the present work. Within the catalyst wall potassium reacts with the V–OH group and turns the active sites to –V–O–K and through surface diffusion these are distributed throughout the wall.

Our results from the bench-scale reactor show that deactivation of SCR catalyst by KCl aerosol is faster than that by K_2SO_4 aerosol. However, our lab-scale investigation of the SCR catalyst deactivation by wet impregnation showed that K_2SO_4 is only a slightly weaker poison compared to KCl [8]. For potassium in the form of aerosol, the different mobility (Tamman and Hüttig temperature)

of KCl and K_2SO_4 could be the reason for the difference between the deactivations caused by KCl and K_2SO_4. For KCl the $T_{Hüttig}$ and T_{Tamman} temperatures are 40 °C and 249 °C and for K_2SO_4 the temperatures are 129 °C and 397 °C, respectively. This implies that the mobility of KCl is larger than K_2SO_4 and therefore penetrates the catalyst faster. Another reason could be that the mass mean diameter of K_2SO_4 aerosols were higher than that of KCl aerosols. The bigger particles have more difficulty to penetrate into the catalyst and also less is deposited.

4. Conclusions

Deactivation of a commercial type V_2O_5-WO_3-TiO_2 catalyst was investigated by exposing the catalyst plates to a layer of KCl particles or ash at a lab-scale reactor and full-length monolith catalysts at a bench-scale reactor with pure KCl or K_2SO_4 aerosols.

Slow deactivation (about 10%) was observed for catalyst plates exposed to a layer of KCl particles at 350 °C for 2397 h with SO_2 addition for 670 h. After 1970 h, no deactivation was found for catalyst plates exposed to ash collected from a SCR pilot plant installed at a straw-fired power plant. SEM-EDX analysis showed that potassium penetrated only about 10% of the catalyst thickness from the contacting surface of KCl but no potassium on the surface and in the structure of the catalyst plates exposed to ash was found.

A fast deactivation was observed for catalysts exposed to pure KCl or K_2SO_4 aerosols at 350 °C in the bench-scale reactor. The deactivation rates for KCl and K_2SO_4 aerosols exposed catalysts were about 1% per day and 0.4% per day, respectively. Deactivated samples were characterized by BET, Hg-porosimetry, SEM-EDX, NH_3 chemisorption. SEM analysis revealed that potassium partly deposited on the catalyst outer wall which may have slightly decreased the diffusion rate of NO and NH_3 into the catalyst. However, potassium also penetrated into the catalyst wall and the average K/V ratios (0.5–0.75) in the catalyst structure were high enough to explain most or all of the activity loss by chemical deactivation. Chemical poisoning was further supported by ammonia chemisorption measurements showing that the amount of chemisorbed NH_3 on the catalyst decreased as a function of exposure time, which reveals that Brønsted acid sites had reacted with poison and rendered inactive. Overall, the conclusion is that chemical poisoning of active sites is the main cause of the deactivation while physical blocking of the outer wall surface area also contribute to the loss of activity. The results support our previous conclusion that the deactivation of SCR catalyst exposed to potassium-containing aerosols is caused by diffusion of fine potassium-containing aerosol into the catalyst pores, and subsequent diffusion into the structure, for example by surface diffusion.

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